77 Rec'd PCT/PTO 17 DEC 2001

ATTORNEY'S DOCKET NO: **011474**

U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE	DATE: **December 17, 2001**
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371	U.S. APPLN. NO. (if known): 09/926764

INTERNATIONAL APPLICATION NO.: **PCT/JP00/03982**	INTERNATIONAL FILING DATE: **JUNE 16, 2000**	PRIORITY DATE CLAIMED: **JUNE 18, 1999**

TITLE OF INVENTION: ***ORGANIC-INORGANIC COMPOSITE MAGNETIC MATERIAL AND METHOD FOR MANUFACTURING SAME***

APPLICANT(S) FOR DO/EO/US: **Tadashi SUGAWARA, Akira IZUOKA and Hiromi SAKURAI**

Applicant hereby submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. XX This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. ___ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. XX This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the time limit set in 35 USC 371(b) and PCT Articles 22 and 39(1).

4. XX A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. XX A copy of the International Application as filed (35 U.S.C. 371(c)(2)):

    a. ___ is transmitted herewith (required only if not transmitted by the International Bureau).
    b. XX has been transmitted by the International Bureau.
    c. ___ is not required, as the application was filed in the United States Receiving Office (RO/US)

6. XX A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. XX Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))

    a. ___ are transmitted herewith (required only if not transmitted by the International Bureau).
    b. ___ have been transmitted by the International Bureau.
    c. ___ have not been made; however, the time limit for making such amendments has NOT expired.
    d. XX have not been made and will not be made.

8. ___ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. ___ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. XX A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

ITEMS 11. TO 16. BELOW CONCERN OTHER DOCUMENT(S) OR INFORMATION INCLUDED:

11. XX An Information Disclosure Statement under 37 CFR 1.97 and 1.98 with 9 references.

12. ___ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
ASSIGNEE NAME AND ADDRESS: ***JAPAN SCIENCE AND TECHNOLOGY CORPORATION, Kawaguchi-shi, Japan***
Please publish the assignee data with the application.

13. XX A **FIRST** preliminary amendment.
___ A **SECOND** or **SUBSEQUENT** preliminary amendment

14. ___ A substitute specification.

15. ___ A change of power of attorney and/or address letter.

16. XX Other items or information: 4 sheets of drawings.

U.S. APPLICATION NO. (if known) 09/926764	INTERNATIONAL APPLICATION NO. **PCT/JP00/03982**	DATE: **December 17, 2001**

17. X The following fees are submitted:	CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5): Search Report has been prepared by the EPO or JPO: $890.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) $710.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $740.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1040.00		
International preliminary examination fee (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$ 890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than __ 20 x 30 months from the earliest claimed priority date (37 DVR 1.492(e)).	**$ 130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
TOTAL	10 -20 =		X $ 18.00		
INDEPENDENT	3 - 3 =		X $ 84.00		
Multiple dependent claims(s) (if applicable)			+ $280.00	**$ 280.00**	
TOTAL OF ABOVE CALCULATIONS =				**$1,300.00**	
Reduction by 1/2 for filing by small entity, if applicable. (Note 37 CFR 1.9, 1.27, 1.28).					
SUBTOTAL =				**$1,300.00**	
Processing fee of **$130.00** for furnishing the English translation later than __ 20 __ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +					
TOTAL NATIONAL FEE =				**$1,300.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00 per property +**					
TOTAL FEES ENCLOSED =				**$1,300.00**	
				Amount to be: refunded	**$**
				charged	**$**

09/926764 04 JC05 Rec'd PCT/PTO 17 DEC 2001

ATTORNEY'S DOCKET NO: **011474**

U.S. APPLICATION NO. (if known)	INTERNATIONAL APPLICATION NO.	DATE: **December 17, 2001**
09/926764	**PCT/JP00/03982**	

a. XX A check in the amount of $1,300.00 to cover the above fees is enclosed. ($890.00 for basic filing fee; $130.00 for late filing of the declaration and $280.00 for multiple dependent claims). (This paper is filed in triplicate)

b. ___ Please charge my Deposit Account No. 01-2340 in the amount of $___ to cover the above fees. (A duplicate copy of this sheet is enclosed.)

c. X The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-2340.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed to request that the application be restored to pending status.

Send All Correspondence To:

23850
PATENT TRADEMARK OFFICE

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of: **Tadashi SUGAWARA et al.**

Serial Number: **Not Yet Assigned**
(PCT/JP00/03982)

Filed: **December 17, 2001**

For: **ORGANIC-INORGANIC COMPOSITE MAGNETIC MATERIAL AND METHOD FOR MANUFACTURING SAME**

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

December 17, 2001

Sir:

Prior to calculation of the filing fee and examination of this application, please amend the above-identified application as follows:

IN THE CLAIMS:

Please amend the claims as follows:

1. (Amended) A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the step of synthesizing an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said synthesizing step includes the steps of:

as said ligands to be formed by chemisorbing thiol on said metal particle, preparing stabilizing ligands chemisorbed on said metal particle; and

subsequently, substituting said stabilizing ligands with thiol-substituted organic radicals each having an unpaired electron.

2. (Amended) A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the step of synthesizing an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said synthesizing step includes the step of:

reducing hydrogen tetrachloroaurate acid with a reducing agent in the presence of a thiol-substituted π-conjugated organic radical having a long-chain alkyl group or any derivatives thereof to directly synthesize the organic-radical chemisorbed gold particle.

3. (Amended) An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2.

4. (Amended) An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2, and

adding a bridging ligand having aπ-conjugation system to provide an enhanced magnetic interaction between said particles in the course of forming the film.

5. (Amended) An organic-inorganic composite magnetic thin-film produced by dissolving the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2, in an organic solvent by themselves or with a bridging ligand having aπ-conjugation system, and then coating the resulting solution on a substrate.

Please **ADD** the following new claims:

6. An organic-inorganic composite magnetic material comprising a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals.

7. An organic-inorganic composite magnetic material as defined in claim 6, wherein each of said unpaired electrons of said thiol-substituted organic radicals is chemisorbed on said metal particle through a π-conjugation so as to provide a magnetic interaction to said metal particle.

Tadashi SUGAWARA et al. Docket No. 011474

REMARKS

The above amendment to the claims has been made to incorporate the amendment under PCT Article 34 (2)(b).

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "Version with Markings to Show Changes Made."

In the event that any fees are due in connection with this paper, please charge our Deposit Account No. 01-2340.

Respectfully submitted,

ARMSTRONG, WESTERMAN, HATTORI,
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VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS

Claims 1-5 have been amended as follows:

1. (Amended) A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the step of synthesizing an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said synthesizing step includes the steps of:

~~reducing a salt including a metal ion with a reducing agent in the presence of a chemically stabilizing ligand so as to form a soluble metal particle, said metal allowing thiol to be absorbed thereon,~~ as said ligands to be formed by chemisorbing thiol on said metal particle, preparing stabilizing ligands chemisorbed on said metal particle; and

subsequently, substituting said stabilizing ~~ligand absorbed on said formed soluble metal particle~~ ligands with a thiol-substituted organic ~~radical~~ radicals each having an unpaired electron ~~so as to synthesize an organic-radical absorbed metal particle~~.

2. (Amended) A method for manufacturing an organic-inorganic composite magnetic material ~~as defined in claim 1, wherein said~~ , said method comprising the step ~~for~~ of synthesizing

an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said systhesizing step includes the step of :

reducing hydrogen tetrachloroaurate with a reducing agent in the presence of a thiol-substituted π-conjugated organic radical having a long-chain alkyl group or any derivatives thereof to directly synthesize the organic-radical chemisorbed gold particle.

3. (Amended) An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed ~~metal~~ gold particles obtained from the method as defined in claim 1 or 2.

4. (Amended) An organic-inorganic composite ~~ferromagnetic~~ magnetic thin-film produced by ~~adding a bridging ligand to~~ using the organic-radical chemisorbed ~~metal~~ gold particles obtained from the method as defined in claim 1 or 2, and adding a bridging ligand having a π-conjugation system to provide an enhanced magnetic interaction between said particles in the course of forming the film.

5. (Amended) An organic-inorganic composite magnetic thin-film produced by dissolving the organic-radical chemisorbed ~~metal~~ gold particles obtained from the method as defined in claim

1 or 2, in an organic solvent by themselves or with a bridging ligand <u>having a π-conjugation system</u>, and then coating the resulting solution on a substrate.

Amendment under PCT Article 34(2)(b)

1. A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the step of synthesizing an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said synthesizing step includes the steps of:

as said ligands to be formed by chemisorbing thiol on said metal particle, preparing stabilizing ligands chemisorbed on said metal particle; and

subsequently, substituting said stabilizing ligands with thiol-substituted organic radicals each having an unpaired electron.

2. A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the step of synthesizing an organic-radical chemisorbed gold particle formed of a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals, wherein said synthesizing step includes the step of:

reducing hydrogen tetrachloroaurate with a reducing agent in the presence of a thiol-substituted π-conjugated organic radical having a long-chain alkyl group or any derivatives thereof to directly synthesize the organic-radical chemisorbed gold particle.

3. An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2.

4. An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2, and adding a bridging ligand having a π-conjugation system to provide an enhanced magnetic interaction between said particles in the course of forming the film.

5. An organic-inorganic composite magnetic thin-film produced by dissolving the organic-radical chemisorbed gold particles obtained from the method as defined in claim 1 or 2, in an organic solvent by themselves or with a bridging ligand having a π-conjugation system, and then coating the resulting solution on a substrate.

New claims

6. An organic-inorganic composite magnetic material comprising a metal particle obtained by applying ligands of thiol-substituted organic radicals each having an unpaired electron to ligands to be formed by chemisorbing thiol on said metal particle so

as to ferromagnetically orient each spin of said unpaired electrons of said organic radicals.

7. An organic-inorganic composite magnetic material as defined in claim 6, wherein each of said unpaired electrons of said thiol-substituted organic radicals is chemisorbed on said metal particle through a π-conjugation so as to provide a magnetic interaction to said metal particle.

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ORGANIC-INORGANIC COMPOSITE MAGNETIC MATERIAL AND METHOD FOR MANUFACTURING SAME

TECHNICAL FIELD

The present invention relates to an organic-inorganic composite magnetic material produced by chemisorbing an organic magnetic material, particularly an organic radical, on the surface of a metal substrate serving as an inorganic component, and a method for manufacturing the same.

BACKGROUND ART

An organic-inorganic composite material related to the present invention includes a gold particle having alkanethiol chemisorbed thereon. This gold particle can be synthesized by adding alkanethiol dissolved in an organic solvent into an ageous solution of hydrogen tetrachloroaurate and then adding a reducing agent in the presence of a surfactant. It is also known that the formed gold particle is desirably stabilized by virtue of the alkanethiol chemisorbed thereon.

Heretofore, various developments concerning functionalized gold particles having organic ligands have been attempted by taking advantage of the self-assembling property of gold particles having alkanethiol chemisorbed thereon (i.e. alkanethiol-chemisorbed gold particles). However, in the developments for functional materials composed of thiol-chemisorbed gold particles, any case focusing on a magnetic material has not been found. Consequently, there has not been any report of

applying thiol-chemisorbed gold particles or other metal particles to a magnetic device as an organic-inorganic composite material.

In terms of the alkanethiol-chemisorbed gold particles as an organic-inorganic composite material, the following reports have heretofore been presented. As for synthesizing method, a report presented by M. Brust et al. describes a method of synthesizing alkanethiol-chemisorbed gold particles by using tetraoctylammonium as a phase transfer catalyst for reducing gold ions to gold in a two-phase system (J. Chem. Soc., Chem. Comm., 801, 1994). A report presented by K. V. Sarathy et al. describes that when gold ions are reduced by tetrakis (hydroxymethyl) phosphonium chloride and the ligand of the gold ions are then exchanged with dodecane thiol in an organic phase under acidic condition, clusters having a uniformed size (about 5 nm) are formed in a regular structure (Chem. Comm., 537, 1997).

As for physical property and structure are concerned, a report presented by R. H. Terrill et al. describes a result of the experimental in which thiols, each having a different alkyl chain length, are absorbed on gold particles and their solid-state properties are then measured (J. Am. Chem. Soc., 117, 12537, 1995). A report presented by M. Brust et al. describes conductive behavior of gold particles coated with dithiol by use of transmission electron micrograms showing structured gold particles (Adv. Mater., 7, 795, 1995). A report presented by S. Chen et al. describes conductive behavior of gold-thiol nanoparticles having different sizes by use of a scanning tunneling microscope (Science, 208, 2098, 1998). Further, a report presented by R. P. Anders et al. describes that when an I-V curve is measured by a scanning tunneling microscope after dithiols are arranged on (111) surface of gold and gold nanoparticles are then absorbed thereon, and that a Coulomb staircase based on single-electron tunneling derived from the sample has been

observed (Science, 272, 1323, 1996). The aforementioned reports relate the synthesizing methods, electrical properties and self-assembled systems of gold particles.

As described above, various developments concerning functionalized gold particles having organic ligands have been attempted by taking advantage of the self-assembling property of gold particles. For example, Japanese Patent Laid-Open Publication No. Hei 09-278598 discloses a micelle type metal particle in which ansphiphilic organic material is absorbed on the surface of a metal particle to cover the particle in the form of a micellar structure, and applicability of this particle to metal particle materials, metal coating materials, gel particle materials, ultra-thin metal film producing apparatuses, optical-energy converting apparatuses or the like.

As described in Japanese Patent Laid-Open Publication No. Hei 06-45142, there is known a magnetic film being an organic film in which molecules forming a monomolecular film or built-up film is fixed directly or indirectly with a substrate through at least one of atoms selected from the group consisting of Si, Ge, Sn, Ti, Zr and Sc in the form of covalent binding, wherein the organic film includes unpaired electrons derived from a metal and/or radical, and exhibits magnetism. However, it would appear that the magnetic film has a critically weak magnetic interaction between the unpaired electrons because the metal and/or radical are bound through saturated hydrocarbon chains.

DISCLOSURE OF INVENTION

In view of the above problem, it is therefore an object of the present invention to provide a method for manufacturing an organic-inorganic composite magnetic material having super-paramagnetism or ferromagnetism, and to open the way for applying organic materials to magnetic devices.

Given that a gold particle is a molecule, the gold particle may be used as a constituent molecule of a nanospin device. Based on this assumption, the inventors have introduced organic radicals into thiol to be chemisorbed on a gold particle, and investigated a magnetic interaction between conduction electrons and localized spins of the radicals, and finally achieved the present invention.

Specifically, the present invention provides a method for manufacturing an organic-inorganic composite magnetic material in which organic radical molecules, each having a localized spin derived from an unpaired electron of the radical, are chemisorbed on the surface of a metal substance, wherein the respective localized spins of the organic radicals are ferromagnetically oriented by a magnetic interaction with conduction electrons of the metal substance.

The metal substance may be made of any metal capable of chemisorbing thiol thereon, such as Au (gold), Ag (silver), Pt (platinum), Pd (palladium), Rh (rhodium), Ru (ruthenium) or the like, and any alloy thereof. By coexisting such a metal substance with radicals each having a thiol group and any derivatives thereof, the organic radicals can be absorbed on the surface of the metal substance. For example, when the metal substance is made of gold, an organic-inorganic composite magnetic material composed of organic-radical chemisorbed gold particles each having thiol-substituted organic-radical molecules chemisorbed on the surface of the gold particle can be obtained.

Preferably, the organic radical is phenyl nitronyl nitroxide having a thiol group in its para position or any derivatives thereof, or phenyl nitroxide having a thiol group in its meta position or any derivatives thereof. However, the radical ligand in question is not limited to a radical having a thiol group as a substituent. For example, a radical having a

substituent derived from disulfide or thiocarboxylic acid capable of being chemisorbed on the metal substance may be used.

The present invention also provides a method for manufacturing an organic-inorganic composite magnetic material, comprising the steps of reducing a metal salt with a reducing agent in the presence of a stabilizing ligand so as to form a soluble metal particle, and substituting the stabilizing ligand absorbed on the formed soluble metal particle with a thiol-substituted organic radical having an unpaired electron so as to synthesize an organic-radical absorbed metal particle. An applicable stabilizing ligand may include any ligand, such as alkanethiol, aromatic thiol, quaternary ammonium salt, quaternary phosphonium salt, polymers having a metal ligand as a side-chain, capable of providing a desired stabilization for preventing metal particles from assembling.

For synthesizing an organic-radical chemisorbed gold particle, it is preferable that hydrogen tetrachloroaurate is reduced with a reducing agent in the presence of a thiol-substituted organic radical having a long-chain alkyl group or any derivatives thereof to directly synthesize the organic-radical chemisorbed gold particle.

Furthermore, the present invention provides an organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed metal particles obtained from the aforementioned method, and an organic-inorganic composite ferromagnetic thin-film produced by adding a bridging ligand in the course of forming the film using the same metal particles.

Preferably, the organic-radical chemisorbed metal particles obtained from the aforementioned method is dissolved in an organic solvent by themselves or with a bridging ligand during its self-condensation, and the resulting solution is coated on a substrate to form an organic-inorganic composite magnetic thin-film. An applicable

coating process may include a spin-coating process or a water-surface condensation process in which the film is self-condensed on a water surface.

Differently from prior arts, in the organic-inorganic composite magnetic material obtained from the manufacturing method according to the present invention, each of the unpaired electrons in the thiol-substituted organic radicals is chemisorbed directly on the metal particle through a π-conjugating bonds. This provides a desirable feature of creating a strong magnetic interaction between the chemisorbed radicals through the conduction electrons of the metal particle.

A desirable magnetism can be yielded to a nonmagnetic fine material having electrical conductivity by adding thiol-substituted radicals. In the resulting magnetic material, by virtue of the interaction with the conduction electrons in its metal substance, the respective unpaired electrons on the radicals are oriented in the same direction to achieve a ferromagnetic spin-arrangement. In particles each having conduction electrons, the unpaired electrons on each of the particles are ferromagnetically oriented to exhibit ferromagnetism. However, the magnitude of the resulting ferromagnetism is not uniformed between the particles. This non-uniformity can be eliminated by adding a bridging ligand having thiol groups at both ends to conjugate the electronic structures between the particles. Thus, the unpaired electrons can be uniformly oriented between the particles to provide a desirable ferromagnetic thin-film.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a schematic diagram of a gold particle having radicals absorbed thereon.

Fig. 2 is a conceptual diagram showing a process for chemically modifying a metal surface by use of thiol-substituted organic radicals.

Fig. 3 is an EPR (Electron Paramagnetic Resonance) spectrum of an organic-radical chemisorbed particle (solid).

Fig. 4 is a graph showing temperature dependence of an EPR signal intensity and a line width of an organic-radical chemisorbed particle.

Fig. 5 is a graph showing temperature dependence of a product ($X_{para} \cdot T$) derived from multiplying a magnetic susceptibility by a temperature of an organic-radical chemisorbed particle.

Fig. 6 is a schematic diagram of an ultra thin-film composed of particles exhibiting a ferromagnetic spin-arrangement, wherein Fig. 6 (a) illustrates a super-paramagnetic ultrathin-film, and Fig. 6 (b) illustrates a ferromagnetic ultrathin-film provided by conjugating the particles with bridging ligands.

Fig. 7 shows formulas 1, 2 and 3 in a manufacturing method of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

With reference to the drawings, an embodiment of the present invention will now be described in connection with an example using gold as a metal substance. Fig. 1 shows a model of a radical-absorbed gold particle serving as a magnetic material. This organic-radical chemisorbed gold particle can be synthesized according to a reaction path as shown in the formuli 1 and 2 of Fig. 7.

Specifically, hydrogen tetrachloroaurate is first reduced with a reducing agent in the presence of quaternary ammonium salt, alkanethiol or the like to synthesize a gold particle 1 stabilized by ligands. Then, organic radicals 2 each having thiol or any derivatives thereof as a substituent are added to undergo an exchange reaction of the ligands with the organic radicals so as to synthesize a gold particle 3 having the organic radicals chemisorbed thereon.

The radical ligand is not limited to thiol, and disulfide derivatives or thiocarboxylic acid derivatives capable of being chemisorbed on a metal substance may be used.

It is believed that thiol absorbed on gold typically exists as thiolate. Since a radical composed of thiolate and phenyl nitronyl nitroxide is a spin polarization donor, once this radical is chemisorbed on the gold particle, the radical polarizes the conduction band of the gold particle. This allows all of localized electrons to be ferromagnetically aligned.

(Example)

A synthesizing method and a magnetic property of a chemisorbed gold particle will further be described in detail based on examples.

<u>Example 1</u>

[Synthesizing Method of Organic-Radical Absorbed Magnetic Gold Particles]

A synthesis was conducted according to the formula 3 shown in Fig. 3. Specifically, 1.0 g (2.4 mmol) of hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$) was dissolved in 30 mL of dry tetrahydrofuran (THF). Then, after adding 0.54 mL (7.3 mmol) of ethanethiol, the solution was stirred under nitrogen atmosphere. 50 mL of THF

solution (1.0 mol /L) including triethyllithium borohydride ($LiEt_3BH$) was dripped into the reaction solution for about 30 minutes while cooling the reaction solution in an ice bath.

After completing the drip of the reducing agent (triethyllithium borohydride), the ice bath was detached, and the solution was stirred one night at room temperature. During this process, the complex of hydrogen tetrachloroaurate and ethanethiol was reduced, and consequently gold particles having ethanethiol chemisorbed thereon were formed.

In order to separate the particles from inorganic ions in the solution by depositing the particles, 2 mL of ethanol and 10 mL of ice water were added. After stirring for one hour, a black power-type deposit was separated through filtration. The obtained black solids were suspended in 30 ml of toluene, and 0.2 mL of ethanethiol was added therein. After stirring the suspension for five minutes, 18 mL of methylene chloride solution including 164 mg (0.32 mmol) of radical disulfide having a structure designated as the numeral 4 in the formula 3 was added therein. After several minutes, gold particles (black solids) each having thiol-substituted organic radicals chemisorbed thereon were deposited. The deposited gold particles were then isolated.

By adding the thiol-substituted organic radicals in the form of disulfide to the deposited gold-alkanethiol particles, an exchange reaction including an oxidation-reduction process yielded organic-radical chemisorbed gold particles. In this process, if thiol-substituted organic radicals each having a long alkyl chain are used, these radicals can be chemisorbed directly on each of the gold particles without the aid of the ethanethiol.

[Magnetic Property of Organic-Radical Chemisorbed Magnetic Gold Particles]

As shown in Fig. 3, an electron paramagnetic resonance (EPR) spectrum of the black-solid radical-chemisorbed magnetic gold particles at room temperature shows an absorption ($g = 1.947$, $\Delta H_{pp} = 36$ mT) having a wide half bandwidth derived from the radical-chemisorbed gold particles. Moreover, as shown in Fig. 4, temperature dependence of the absorption intensity (signal intensity) shows a Curie paramagnetic behavior at the temperature ranging from 20 K to 200 K. In addition, it is characteristic that the line width of the absorption spectrum is proportional to the reciprocal of the temperature value.

Fig. 5 shows temperature dependence of the magnetic susceptibility (X_p) determined by subtracting a temperature-independent magnetic susceptibility (components of diamagnetism, Pauli paramagnetism, ferromagnetism and the like) in the measurement of the magnetic susceptibility of the same sample as described above by use of a superconducting quantum interference device (SQUID). The broken line shows a Curie constant on the assumption that no magnetic interaction exists between organic radicals in a sample including gold and organic radicals at the ratio of 3:1.

As shown in Fig. 5, the Curie constant and the Weiss temperature are analyzed as 3×10^{-3} emuK / gram and -2.5 K, respectively. Based on this Curie constant, an average spin quantum number of about 8 ± 3 is determined. This proves that the average number, about sixteen of the organic radicals absorbed on each one of the gold particles are ferromagnetically oriented with uniformed spin directions at room temperature.

Thus, the above measurement result of this example can be considered as evidence of the desired formation of the organic-radical chemisorbed gold particles exhibiting super-paramagnetism as shown in Fig. 6 (a). In this sample, the size of the

gold particles and the number of the organic radicals chemisorbed on each one of the gold particles have a certain distribution. Thus, the spin quantum number also shows a certain distribution.

A magnetic gold particle chemisorbing thiol-substituted organic radials each having a long-chain alkyl group is soluble in an organic solvent. Thus, a magnetic thin-film can be produced by subjecting a solution of the magnetic gold particles to the spin coat process, or the water-surface condensation process in which the solution is suspended on a water surface and then the solvent is vaporized to assemble the gold particles on the water surface. The resulting thin film exhibits super-paramagnetism as the solid sample. Further, by adding bridging ligands to the organic solvent, a ferromagnetic thin film having the perfectly aligned direction of spins on the gold particles can be produced as shown in Fig. 6 (b).

INDUSTRIAL APPLICABILITY

As described above, the present invention provides a composite material of organic radical molecules and a metal substance serving as an inorganic component, and in particular, realizes a super-paramagnetic material by utilizing a magnetic interaction between unpaired electrons of the organic radicals and conduction electrons of the metal substance to orient the unpaired electrons of the organic radicals ferromagnetically. Further, the present invention provides a novel organic-inorganic composite ferromagnetic material by conjugating these super-paramagnetic metal particles through bridging ligands to form a thin film exhibiting ferromagnetism.

An applicable form of the metal substrate may include a metal thin-film, nanometer level of particle, micro-fabricated metal wire, or electrode pattern. Thus, the magnetic

material according to the present invention can be extensively used in magnetic devices of various microelectronic devices.

What is claimed is:

1. A method for manufacturing an organic-inorganic composite magnetic material, said method comprising the steps of:

reducing a salt including a metal ion with a reducing agent in the presence of a chemically stabilizing ligand so as to form a soluble metal particle, said metal allowing thiol to be absorbed thereon, and

substituting said stabilizing ligand absorbed on said formed soluble metal particle with a thiol-substituted organic radical having an unpaired electron so as to synthesize an organic-radical absorbed metal particle.

2. A method for manufacturing an organic-inorganic composite magnetic material as defined in claim 1, wherein said step for synthesizing an organic-radical chemisorbed gold particle includes the step of reducing hydrogen tetrachloroaurate with a reducing agent in the presence of a thiol-substituted organic radical having a long-chain alkyl group or any derivatives thereof to directly synthesize the organic-radical chemisorbed gold particle.

3. An organic-inorganic composite magnetic thin-film produced by using the organic-radical chemisorbed metal particles obtained from the method as defined in claim 1 or 2.

4. An organic-inorganic composite ferromagnetic thin-film produced by adding a bridging ligand to the organic-radical chemisorbed metal particles obtained from the method as defined in claim 1 or 2, in the course of forming the film.

5. An organic-inorganic composite magnetic thin-film produced by dissolving the organic-radical chemisorbed metal particles obtained from the method as defined in claim 1 or 2, in an organic solvent by themselves or with a bridging ligand, and then coating the resulting solution on a substrate.

ABSTRACT

The present invention provided a method for manufacturing an organic-inorganic composite magnetic material which has organic radical molecules chemisorbed on the surface of a metal substance and exhibits super-paramagnetism or ferromagnetism. An ionic salt of a metal allowing thiol to be absorbed thereon is reduced with a reducing agent in the presence of a stabilizing ligand so as to form a soluble metal particle. The stabilizing ligand absorbed on the formed soluble metal particle is exchanged with a thiol-substituted organic radical having an unpaired electron so as to synthesize an organic-radical absorbed metal particle.

Fig. 1

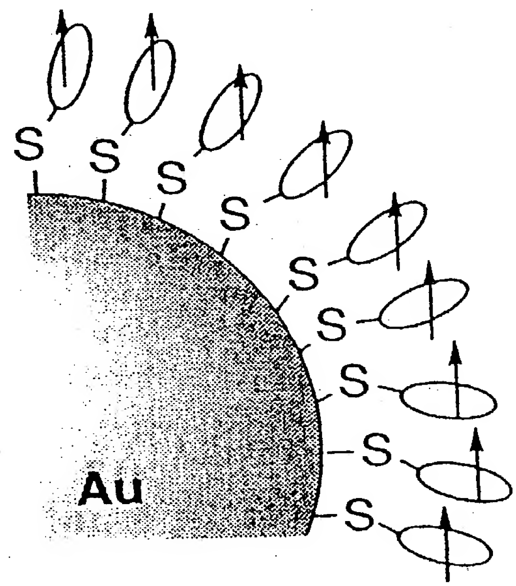

S
Au

Fig. 2

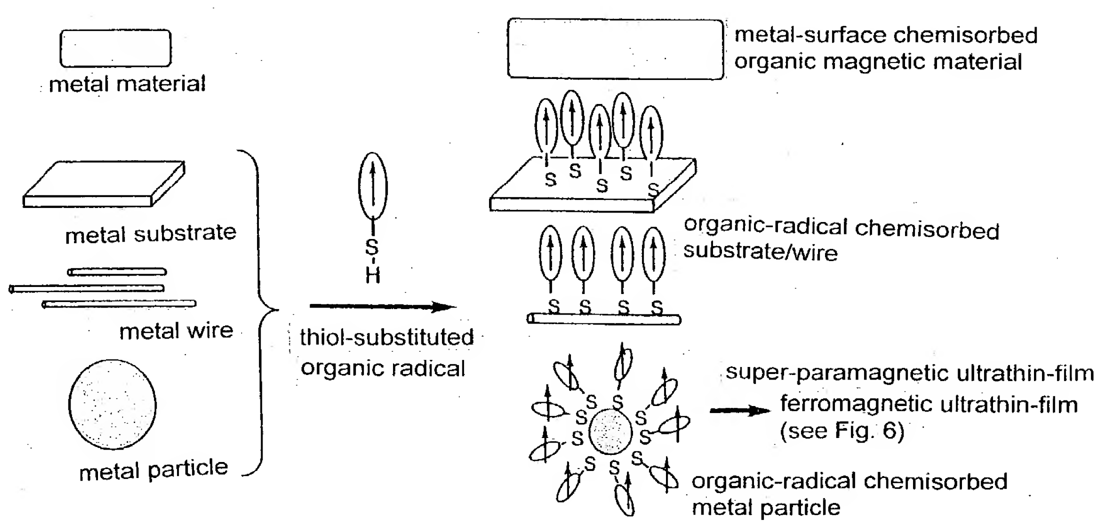
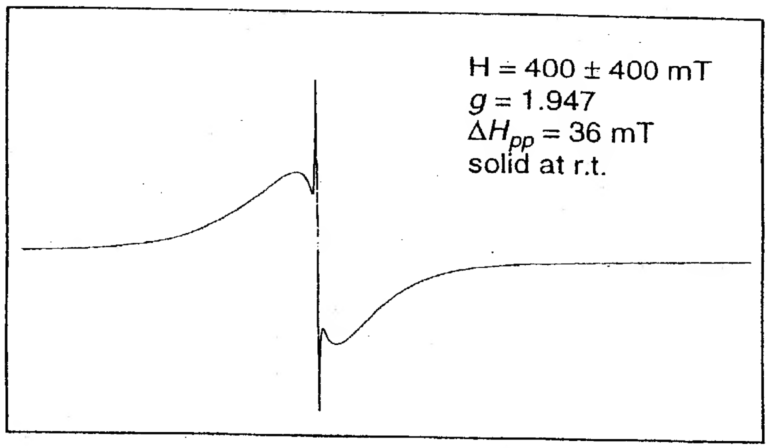

metal material
metal substrate
metal wire
metal particle
S
H
thiol-substituted
organic radical
metal-surface chemisorbed
organic magnetic material
organic-radical chemisorbed
substrate/wire
super-paramagnetic ultrathin-film
ferromagnetic ultrathin-film
(see Fig. 6)
organic-radical chemisorbed
metal particle

Fig. 3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g = 1.947
ΔHpp = 36 mT
solid at r.t.

Fig. 4

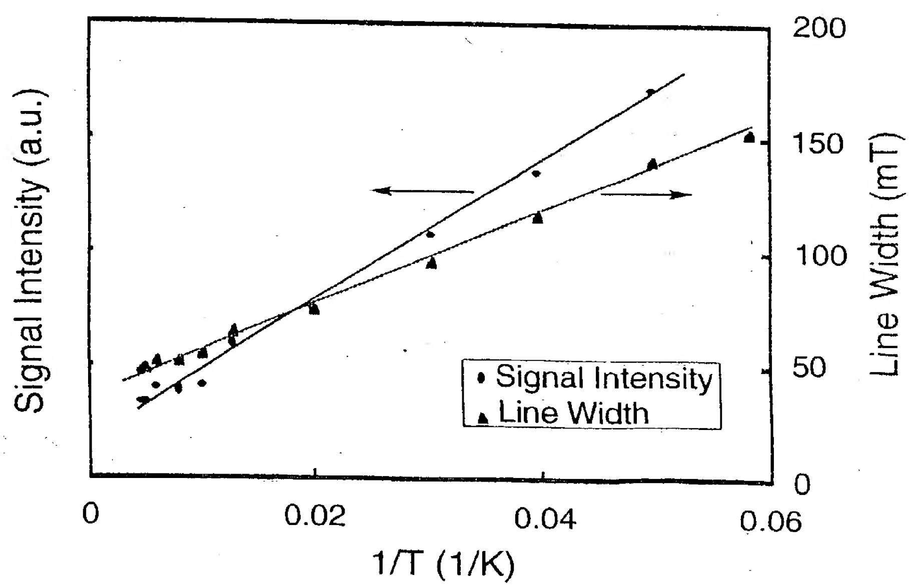

Signal Intensity (a.u.)
Line Width (mT)
200
150
100
50
0
0
0.02
0.04
0.06
1/T (1/K)
Signal Intensity
Line Width

Fig. 5

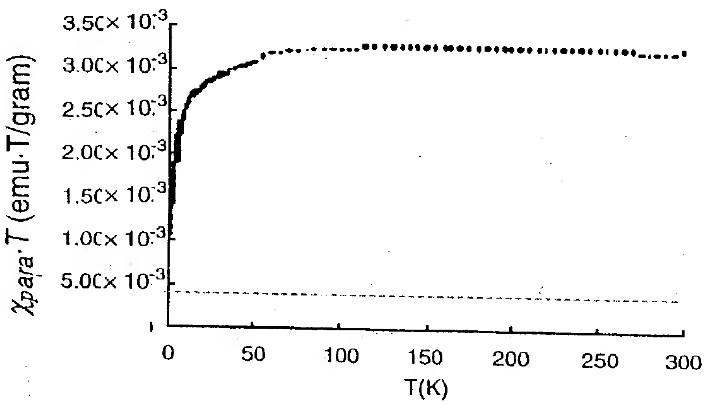

3.50× 10⁻³
3.00× 10⁻³
2.50× 10⁻³
2.00× 10⁻³
1.50× 10⁻³
1.00× 10⁻³
5.00× 10⁻³
$\chi_{para} \cdot T$ (emu·T/gram)
0
50
100
150
200
250
300
T(K)

Fig. 6

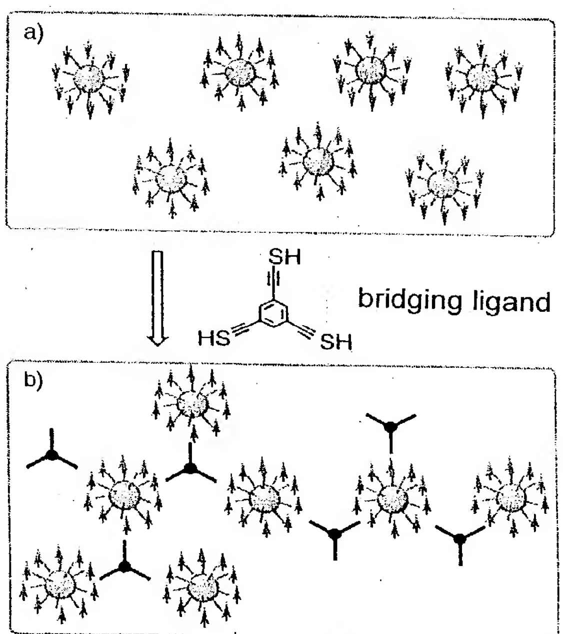
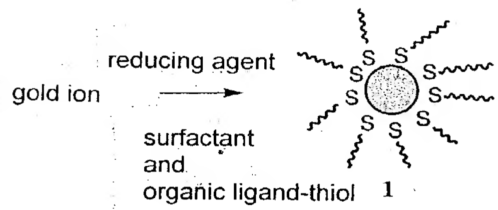
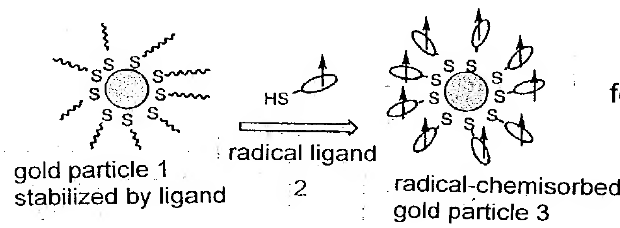

a)
SH
HS
SH
bridging ligand
b)

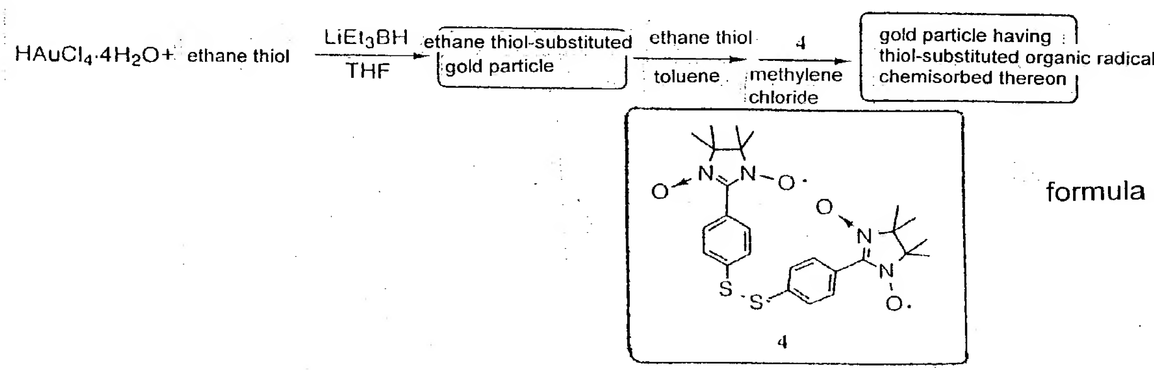
Fig. 7



formula 1



formula 2



formula 3

Docket No. ____________

ARMSTRONG, WESTERMAN, HATTORI, McLELAND & NAUGHTON, LLP

Declaration for U.S. Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention **entitled** (Insert Title) **ORGANIC-INORGANIC COMPOSITE MAGNETIC MATERIAL AND METHOD FOR MANUFACTURING SAME**

the specification of which is attached hereto unless the following is checked

G was filed on **June 16, 2000** as United States Application Number or PCT International Application Number **PCT/JP00/03982** and was amended on ____________ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claim(s), as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, ' 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, ' 119 (a) - (d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application for which priority is claimed:

(List prior foreign applications. See note A on back of this page)	(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed
	11-173395	Japan	18/June/1999	X Yes ___ No
				___ Yes ___ No
				___ Yes ___ No
				___ Yes ___ No

(See note B on back of this page) __ See attached list for additional prior foreign applications

I hereby claim the benefit under Title 35, United States Code, ' 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, ' 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, ' 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(List Prior U.S. Applications)	(Appln. Serial No.)	(Filing Date)	(Status: Patented, Pending, Abandoned)
	(Appln. Serial No.)	(Filing Date)	(Status: Patented, Pending, Abandoned)
	(Appln. Serial No.)	(Filing Date)	(Status: Patented, Pending, Abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

23850

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PATENT TRADEMARK OFFICE

09926764 .040902

Please direct all communications to the following address: *23850*

23850

PATENT TRADEMARK OFFICE

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18 of the United States Code, ' 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Full name of fourth inventor (given name, family name) ______

Inventor's signature ______ Date ______

Residence ______ Citizenship ______

Post Office Address ______

Full name of fifth inventor (given name, family name) ______

Inventor's signature ______ Date ______

Residence ______ Citizenship ______

Post Office Address ______

Full name of sixth inventor (given name, family name) ______

Inventor's signature ______ Date ______

Residence ______ Citizenship ______

Post Office Address ______

Rev. 11/00

NOTES

A. Please list all foreign applications relating to the invention and check block "yes" or "no".

B. If more than 4 prior foreign applications, please check this box and attach a sheet listing the remaining prior foreign applications.

C. For residence in the U.S., indicate city and state, for residence outside the U.S., indicate city and country. The "Post Office Address" must be an address acceptable by a Post Office for delivery of mail.